## **EFFECT OF ANNEALING TIME-TEMPERATURE CONDITIONS ON THE CORROSION RESISTANCE OF ELECTROLESS Ni–P COATINGS**

*L. DZIB-PEREZ* <sup>1</sup> *, O. BILYY* <sup>1</sup> *, A. LEON-GRONIMO* <sup>1</sup> *, J. G. CASTANO-GONZALEZ* <sup>2</sup> *, P. GUINTANA* <sup>3</sup> *, R. DOMINGUUEZ-MALDONADO* <sup>4</sup> *, J. GONZALEZ-SANCHEZ* <sup>1</sup>

<sup>1</sup> Centre for Corrosion Research, Autonomous University of Campeche, México; <sup>2</sup> Centro de Investigación, Innovación y Desarrollo de Materiales, Sede de Investigación Universitaria – SIU, Universidad de Antioquia, Medellín, Colombia; <sup>3</sup> CINVESTAV-Mérida, Applied Physics Department, Mérida, Yucatán, México;

4 División de Ingeniería y Ciencias Exactas, Universidad Anahuac-Mayab, Mérida, Yucatán, México

The purpose of this work is to analyze the effect of different annealing temperature-time processing conditions applied to electroless Ni–P (12 wt.% P) coatings to improve the corrosion resistance in a  $3.5\%$  NaCl solution. An annealing process at 400 $^{\circ}$ C for 4 h applied to electroless Ni–P coatings (12 wt.% P) induces the crystallization of the coating with the formation of stable Ni3P and Ni phases. This crystalline Ni–P coating presents better corrosion resistance in the 3.5 wt.% NaCl solution than the amorphous alloy and the coatings annealed at 400 and  $500^{\circ}$ C for 1 and 2 h. The corrosion resistance of the Ni–P coatings is evaluated by electrochemical impedance spectroscopy for 4 h of immersion. The microstructure of the Ni–P coatings before and after annealing at 400 and 500°C for 1; 2 and 4 h, is studied by X-ray diffraction (XRD) and scanning electron microscopy. Annealing at 400°C for 4 h induces the preferential orientation of the plane (112) of the Ni3P phase as revealed by XRD analysis which modifies the kinetics of the electrochemical reactions. The corrosion resistance of the Ni–P coatings annealed at 400°C for 4 h is related to the formation of texturized  $Ni<sub>3</sub>P$  phase which is chemically stable and comprises 80% of the coating volume.

**Keywords:** *Ni–P coatings, electroless deposition, heat treatment, annealing, corrosion resistance, texture, microstructure, Ni3P phase.* 

Проаналізовано вплив різних температурно-часових умов відпалу на корозійну тривкість хімічно осаджених Ni–P (12 wt.% P) покрить у 3,5%-му розчині NaCl. За відпалу при 400°С упродовж 4 h покриття кристалізуються з утворенням стабільних  $N_i$ -P та Ni фаз. Вони корозійно тривкіші у цьому розчині, ніж аморфний сплав та покриття, відпалені при 400 та 500°C упродовж 1 та 2 h. Корозійну тривкість оцінювали методом електрохімічної імпедансної спектроскопії, а мікроструктуру – методами рентгенівської дифракції і сканувальної електронної мікроскопії. Виявлено, що відпал при 400°C впродовж 4 h викликає переважну орієнтацію фази Ni3P у площини (112), внаслідок чого змінюється кінетика електрохімічних реакцій. Підвищена корозійна тривкість таких покрить зумовлена утворенням текстурованої фази Ni3P, яка хімічно стабільніша і займає 80% об'єму покриття.

**Ключові слова**: *покриття Ni–P, хімічне осадження, термічне оброблення, відпал, корозійна тривкість, текстура, мікроструктура, фаза Ni3P.* 

**Introduction**. Electroless deposition of nickel alloys has been widely applied to surface processing to provide wear resistance, low friction coefficient, non-magnetic behaviour, and high corrosion resistance to engineering components and structures [1, 2].

Corresponding author: J. GONZALEZ-SANCHEZ, e-mail: jagonzal@uacam.mx

It is shown that electroless Ni–P coatings are deposited with uniform thickness all over the object plated regardless of the geometric complexity of the substrate surface [3]. Corrosion resistance of Ni–P electroless coating in common aggressive environments is a function of its phosphorous content. When studying the coating time and heat treatment of electroless Ni–P coatings in [4] it is reported that coatings containing from 11.1 to 13.1% phosphorous are amorphous, and more resistant to corrosion attack than microcrystalline coatings. It is also shown that the heat-treated Ni–P coating with 11.7 and 12.2% P demonstrates a lower corrosion rate than the samples with a phosphorous content of 10.1 and 10.8%.

Annealing treatment was applied to auto-catalytic Ni–P coatings at temperatures from 230 to 400°C and the transformation from amorphous to crystalline microstructure with clear XRD peaks related to the  $Ni<sub>3</sub>P$  and Ni phases when annealed at 400 $^{\circ}$ C was observed [5]. On the other hand, the heat-treated samples at  $230^{\circ}$ C for 2 h underwent negligible changes in their microstructure mainly due to the small-scale crystallization. These authors reported a detrimental effect of the annealing heat treatment on the corrosion resistance of electroless Ni–P coatings. Also, in [6] it was shown that crystalline Ni–P coatings did not passivate in chloride-containing electrolytes when subjected to anodic polarization whereas the amorphous Ni–P formed passive layers. Higher corrosion resistance was observed for the annealed ternary electroless Ni–W–P alloy than the amorphous counterpart in aerated acidic solution. This study clarifies that electroless Ni–P coatings containing 12 wt.% P subjected to annealing at 400°C for 4 h have higher corrosion resistance than the coating with amorphous microstructure and coatings subjected to annealing treatments 1 and 2 h at 400 and 500°C [7].

**Experimental.** *Ni–P electroless plating*. AISI 1020 carbon steel disks of 12 mm diameter and 3 mm thickness were used as substrates for the deposition of autocatalytic Ni–P coatings. Before coating, the steel samples were ground with 600 grit SiC abrasive paper, followed by sandblasting, washing with ethanol in an ultrasonic bath for 10 min, dried with hot air and weighed. Then, samples were immersed in the electroless bath at 90°C for 1 h for the autocatalytic deposition of the Ni–P coating. The chemical composition and operating conditions of the bath for the autocatalytic deposition of Ni–P were taken from [8]. The electroless bath used in the present work produced Ni–P coatings with 12 wt.% of P also followed the work [5] to ensure the formation of Ni3P and Ni phases after the annealing treatment at 400°C.

*Annealing heat treatment*. Ni–P coated samples were subjected to annealing heat treatment [9] using a nichrome resistance furnace in a sealed quartz chamber with a controlled atmosphere and a system to ensure vacuum conditions. During the heat treatment, a constant flow of Ar gas was supplied inside the furnace chamber to avoid the oxidation of the sample. The samples were annealed at  $400^{\circ}$ C and  $500^{\circ}$ C for 1; 2 and 4 h from room temperature to the heat treatment temperature with a heating rate of  $10^{\circ}$ C ⋅ min<sup>-1</sup>, after the annealing process the samples were cooled in the furnace at a rate of  $0.5^{\circ}$ C ⋅ min<sup>-1</sup>.

*Surface characterization methods*. The Ni–P coatings in the deposition state and after the annealing heat treatment at 400 and 500°C for 1; 2 and 4 h were subjected to XRD analysis in a diffractometer Bruker D-8 Advance, with  $CuK_{\alpha}$ -radiation and  $\lambda = 1.5418$  Å used in Bragg mode. The sweep step was 0.02 degrees and the sweep time was – 0.3 s. The range of the angle between the incident beam and the diffracted beam (2θ) was from 25° to 85°. The scanning electron microscopy analysis was also applied to the samples with and without annealing heat treatment before and after the electrochemical tests with an XL30 ESEM Phillips microscope, equipped with an EDAX system using the energy of 25 keV and a pressure of 0.4 Torr. The EDX spectra were obtained with a Saphire-SUTW detector at 25 keV energy and 131.93 eV resolutions. The data were analyzed using commercial software in order to determine the crystalline phases present in the samples after the heat treatment. Additionally, the crystallite size was evaluated by the Scherrer formula.

*Electrochemical behaviour*. The electrochemical [10] behaviour associated with the resistance to corrosion degradation of the autocatalytic Ni–P coatings in 3.5 wt.% NaCl solution was determined by Electrochemical Impedance Spectroscopy (EIS) measurements. The Ni–P coated samples in the deposition state and the Ni–P coated samples subjected to the annealing treatment at 400 and 500°C were used as working electrodes with a surface area of 1 cm<sup>2</sup> exposed to the electrolyte in a conventional three-electrode electrochemical cell using a graphite bar (auxiliary electrode) and saturated calomel electrode (reference electrode). The EIS measurements were conducted at a temperature of  $25 + 1^{\circ}$ C applying a sinusoidal potential signal of 20 mV of amplitude scanning in the frequency range from 20 kHz to 50 MHz. The experiments were performed with an electrochemical station Solartron Analytical, model 1280°C controlled by a computer with commercial software in sequences of measurements at intervals of 1 h.

**Results and discussion**. *Surface characterization*. The Ni–P coating surface without heat treatment presented the characteristic hemispherical features of nodular structure, typical of amorphous material, with the appearance of cauliflower-like nodules (Fig. 1*a*). The observed same structure for the electroless Ni–P coating with 11 wt.% phosphorous showed that the coatings had an amorphous microstructure [11]. The elemental mapping analysis carried out on the Ni–P coatings surface demonstrated a homogeneous distribution of phosphorus and nickel (Fig. 1*b*, *c*), respectively.



Fig. 1. The scanning electron microscopy images to  $\times$ 400 (and zoom to  $\times$ 2) of the Ni–P coatings in the deposition condition (*a*) and elemental mapping for P (*b*) and Ni (*c*).

Fig. 2 shows the transverse section of the Ni–P coated samples and profiles of P, Ni and Fe through the thickness of the Ni–P coatings, using the line scan technique. From the intersection of the P and Ni profile with the Fe profile, a thickness of 17  $\mu$ m for the coating was determined. The content of Ni and P on the electroless Ni–P coating, determined using the Energy Dispersive X-Ray Spectroscopy, was 88 and 12%, respectively, which agreed with the reported data [8].



Fig. 2. The scanning electron microscopy image of the transverse section of the Ni–P coatings and elemental profiles parallel to line scan: *1* – oxides on the surface of the Ni–P coating; *2* – Ni–P coating; *3* – base metal: steel (Fe).

*XRD analysis*. The diffraction patterns of the electroless Ni–P coatings in the asplated condition, annealed at 400 and 500°C are shown in Fig. 3. The XRD spectra of the non-annealed Ni–P coatings present a single broad peak in the 2θ windows from 40 to 50 approximately which is an amorphous structure. Upon receipt of the electroless Ni–P coating containing 11.36% P, several research works reported a similar result and associated it with an amorphous Ni–P deposit [12, 13]. It determined an amorphous structure for deposition state of Ni–P coatings with 10 wt.% P [14] and observed the formation of  $Ni<sub>3</sub>P$  after annealing of the coating at 400 $^{\circ}$ C for 1 h.



Fig. 3. The XRD pattern of the electroless Ni–P coatings in the deposition condition (amorphous) and after annealing heat treatment at  $400^{\circ}C(a)$  and  $500^{\circ}C(b)$  for 1; 2 and 4 h:  $\bullet$  – Ni<sub>3</sub>P phase;  $\blacksquare$  – Ni phase;  $\blacktriangle$  – Fe phase.

The samples annealed present several peaks at different diffraction angles 2θ which suggest the transformation from the amorphous to crystalline phases. The XRD pattern indicates the presence of two crystalline phases, Ni and  $Ni<sub>3</sub>P$ , which agrees with the results of [4] where the effect of coating time and heat treatment on the structure and corrosion resistance of Ni–P electroless containing 11.1...13.1% P is investigated. As the annealing time increases to 4 h, the crystallization is complete and can be assumed that the coatings consist of 80% Ni3P and 20% Ni following the Ni–P thermodynamic phase diagram which establishes the co-existence of Ni and Ni3P for alloys with up to 15 wt.% P which is thermodynamically stable up to 870°C. In [15] the same phases in the Ni–P coating with 17 wt.% P after annealing at 450°C for 1 h, are reported, the thermodynamically stable phase is Ni3P. In [16] XRD peaks corresponding to FCC crystalline structure of Ni and Ni*x*P*<sup>y</sup>* when Ni–P electroless coatings were annealed at 400°C for 1 h, suggesting the initiation of the precipitation of the second phase are obtained.

Fig. 4 shows a comparison between the experimental diffraction pattern of Ni–P coated sample annealed at 400 $^{\circ}$ C for 2 h and the diffraction pattern of the Ni<sub>3</sub>P and Ni phases taken from the database of the International Center for Diffraction Data (ICDD).

According to the ICDD, the peak with the highest intensity for  $Ni<sub>3</sub>P$  corresponds to plane (231) at  $2\theta = 41.80$ , whose intensity is proportional to the structure factor. However, for the samples annealed at  $400^{\circ}$ C for 2 and 4 h the peak with the highest intensity for Ni3P corresponds to plane (112). This difference of the peaks intensities suggests a preferential orientation of the crystalline plane, i.e. the sample presents texture. The sample heat-treated at 500°C for 1 h also presents preferential orientation in the plane (112) for Ni<sub>3</sub>P, not so the samples with heat treatment at  $500^{\circ}$ C for 2 and 4 h. This difference is associated with the higher corrosion resistance of the samples annealed at 400 $^{\circ}$ C for 4 h than the coatings annealed at 500 $^{\circ}$ C as will be discussed in the next section.



Fig. 4. ICDD diffraction pattern powder sample (dash lines), experimental pattern from Ni–P coating with 400°C heat treatment for 2 h.

**Electrochemical behaviour**. The results of the EIS measurements at open circuit potential for the Ni–P coatings deposition state, annealed at  $400$  and  $500^{\circ}$ C are shown in Figs. 5–7, respectively. In these figures the experimental data are presented as symbols and the fitted data as lines. The impedance results show a similar tendency for amorphous and annealed coatings at 400 and 500°C for 2 and 4 h, showing a single semi-circle in the high-frequency regions of Nyquist diagrams, which is indicative of a charge transfer controlled reaction. This implies the same corrosion mechanism for the Ni–P coatings, amorphous and annealed, but different corrosion rate, which is associated with the physical characteristics of the surface, such as pore quantity and the net surface area due to the nodular nature which decreases after annealing. In agreement with [12, 16, 17], in this study, a single inflexion point was observed in the Bode plot for the Ni–P coatings in the deposition state, indicating charge transfer controlled reactions. This behaviour was observed also for the samples annealed at 400 and 500°C for 2 and 4 h with only one phase angle maximum close to 85° that is related to a capacitive behaviour. In [18] this behaviour is associated with the capacitive character of the electric double layer (EDL) between the corrosive medium and the Ni–P coating.

The impedance of the coating in the deposition state decreases from 50000 to 35000  $\Omega$ ⋅cm<sup>2</sup> as the immersion period increases from 1 to 4 h. This behaviour corroborates the formation of corrosion products that do not form passive films but dissolved compounds that produce anions such as hypophosphite, adsorbed on the coating.



Fig. 5. Nyquist (*a*) and Bode (*b*) diagrams from Ni–P coating in the as deposited condition (amorphous microstructure) as a function of immersion time in 3.5 wt.% NaCl solution:  $\blacksquare$  – immediately after immersion in the electrolyte;  $\square$  – 1 h;  $\blacksquare$  – 2;  $\square$  – 3;  $\blacktriangle$  – 4 h.

The Nyquist and Bode diagrams in Fig. 6 show that the impedance of the samples annealed at  $400^{\circ}$ C for 1 h is lower than the impedance of coatings in the deposition state and that for samples annealed for 4 h and the corrosion process involves two-time constants.

The samples submitted to heat treatment at  $400^{\circ}$ C for 4 h, present impedance values about 3 times larger than for the coatings without heat treatment and more than 20 times larger than the samples annealed for 1 h. The high corrosion resistance of the Ni–P coating annealed at 400°C for 4 h can be related to the formation of the thermodynamically stable intermetallic  $Ni<sub>3</sub>P$  phase [15]. In [14] it is determined that the annealing treatment at 400°C for 1 h significantly improves the coating density and structure, giving rise to an enhanced corrosion resistance for the Ni–P electroless coatings.

The EIS results, for samples presenting one time constant, were fitting by a simple equivalent circuit as shown in Fig. 8*a* using the Zview analysis software, where  $R_{el}$  is the resistance of the electrolyte,  $CPE_{\text{edl}}$  is a constant phase element, which in this case can be associated with the electric double-layer capacitance of the interphase coatingelectrolyte, and  $R<sub>ct</sub>$  is the charge transfer resistance-associated reactions. Study [16] reports the values of charge transfer resistance ( $R_{\rm ct}$ ) of 13 kΩ⋅cm<sup>2</sup> for Ni–P coatings (10 wt.% P) in the deposition state and from 18 to 53 k $\Omega$ ⋅cm<sup>2</sup> for coatings heat-treated at 400°C, which are very similar to the values reported in the present study. In the present case, the Ni–P coatings contain 12 wt.% P and the  $R_{\rm ct}$  for the deposition state coatings is 35 k $\Omega$ ⋅cm<sup>2</sup>. In [4] the electroless Ni–P alloys for various coating times (i.e., different content of phosphorus) are found to have amorphous-like structure for phosphorus contents above 11%, while coatings with 10.1 and 10.8 wt.% P have essentially microcrystalline structures.

Fig. 8*b* presents the equivalent circuit related to the behaviour of the coatings annealed at 400 $^{\circ}$ C for 1 h, where  $R_{el}$  is the resistance of the electrolyte,  $CPE_{cl}$  is coating layers constant phase element and  $R<sub>cl</sub>$  is coating layers resistance. The charge transfer resistance and the capacitance of the interface substrate-electrolyte are modelled by  $R_{\text{ct}}$ and *CPE*edl, respectively. This was suggested due to the partial crystallization of the Ni–P after 1 h at 400°C. It could induce sites of active Ni that undergo corrosion without passivation. The presences of two capacitive arcs in the Nyquist diagram indicate that the solution has contacted the metal base through the empty spaces of the plating and the corrosion process occurs.

For both annealing temperatures, the  $R_{ct}$  values (Fig. 9*a*), increase for longer annealing periods. The highest values of  $R<sub>ct</sub>$  were for the Ni–P coatings annealed for 4 h at both, 400 and 500°C. Except for the samples annealed for 1 h, the  $R_{\rm ct}$  values obtained

for samples annealed at 400°C were larger than those of coatings annealed at 500°C. In [16] it is found that the  $R_{\text{ct}}$  for Ni–P a coating (10 wt.% P) annealed at 400°C for 1 h, is 53 k $\Omega$ ⋅cm<sup>2</sup> and for samples annealed at 600°C for 0.25 h is 27 k $\Omega$ ⋅cm<sup>2</sup>.





The  $R_{\text{ct}}$  values obtained for coatings annealed for 1 h, at 400 (Fig. 6) and at 500°C (Fig. 7) are lower than those obtained for the sample without heat treatment. These results are associated with the initiation of the transformation from the amorphous to crystalline phase by the effect of heat treatment in the coatings due to the formation of grain boundaries and intermetallic-Ni boundaries.

The improvement of corrosion resistance after heat treatment coincides with that reported by [15]. A similar result for the Ni–P (17 wt.% P) coating after annealing at 420°C is obtained. The author suggests that this electrochemical behaviour is related to the formation of the intermetallic compound Ni3P with high thermodynamic stability.



Fig. 7. Nyquist and Bode diagrams from Ni–P coating annealed at 500°C for 1 (*a*); 2 (*b*) and 4 h (*c*), as a function of immersion time in 3.5 wt.% NaCl solution:  $\blacksquare$ – immediately after immersion in the electrolyte;  $\square$  – 1 h;  $\bullet$  – 2;  $\square$  – 3;  $\blacktriangle$  – 4 h.



According to the XRD results, the samples with Ni–P coating after heat-treatment exhibit abnormal behaviour in the intensities of the crystalline planes that is commonly known as texturing. This suggests that the texture of the coating annealed at 400°C for 4 h is related to the  $R_{\text{ct}}$  improvement. The above is suggested based on the behaviour

shown by the samples annealed at  $400^{\circ}$ C for 4 h (texturized) with a predominant plane (112), compared with samples annealed at 500°C for 1 and 2 h (non-texturized), the first presenting better corrosion resistance.



Fig. 9. The transfer resistance values of Ni–P coating as a function of immersion time in the NaCl solution (*a*) and capacitance values of Ni–P coating, with and without heat treatment, as a function of experiment time (*b*):  $\star$  – not-annealed;  $\Box$ ,  $\Diamond$ ,  $\triangle$  – 400°C for 1 h; 2 h and 4 h, respectively;  $\blacksquare$ ,  $\spadesuit$ ,  $\blacktriangle$  – 500°C for 1 h; 2 h and 4 h, respectively.

Capacitance  $C_{\rm dl}$  values (Fig. 9*b*) were obtained using the  $H_{\rm su}$  and Mansfeld equation [19]. The coatings annealed at 400 and 500°C for 4 h present the lowest values compared with the coatings with the different metallurgical conditions, whereas the coatings annealed for 1 h at both temperatures present the highest capacitance values which is related to poor corrosion resistance. This indicates that microstructural changes caused by the heat treatment time reduce the capacity of the coating-electrolyte interphase to store charge.

The sample heat treatment at 400 and 500°C for 4 h presents the lower capacitance value and the highest  $R_{ct}$ . The small capacitance values suggest that the Ni–P coatings obtain a less porous characteristic after the annealing at 400 and 500°C for 4 h which are almost one order of magnitude lower than those described by [14, 20]. The corrosion resistance of the Ni–P coating (9.0 wt.% P) decreases after annealing at  $450^{\circ}$ C for 1 h. The preferential dissolution of Ni could complete the formation of P rich compounds that give electrochemical stability to the coating.

## **CONCLUSIONS**

Amorphous Ni–P electroless coatings with 12 wt.% P were deposited on a low carbon steel substrate. The effects of annealing treatment at 400 and  $500^{\circ}$ C for 1; 2 and 4 h on the corrosion resistance of the coating were systematically studied. The results show that a proper temperature and holding time of annealing heat treatment can significantly improve the corrosion resistance of 12 wt.% Ni–P coatings when compared with samples with an amorphous structure. Annealing heat treatment at 400°C induces the crystallization of the coatings with the formation of the  $Ni<sub>3</sub>P$  phase that is thermodynamically more stable because of its larger heat of formation than Ni or P in the amorphous coating. Annealing at 400°C for 4 h induces the complete formation of  $Ni<sub>3</sub>P$  and makes the coating less porous because of the lowest values of the  $C<sub>dl</sub>$  and the highest charge transfer resistance compared with the samples with different annealing conditions. After annealing at  $400^{\circ}$ C at 4 h, the crystalline phases develop a texture that changes the electrochemical kinetics; the abundant  $Ni<sub>3</sub>P$ , which is 80% of the volume of the coating, presents a preferential orientation of the plane (112).

- 1. *Sahoo P. and Das S. K.* Tribology of electroless nickel coatings // Materials & Design.  $-2011$ .  $-32$ ,  $\mathbb{N}$  4.  $-2011$ .  $-$  P. 1760–1775.
- 2. *León-Patiño C.A., García-Guerra J., and Aguilar-Reyes E. A.* Tribological characterization of heat-treated Ni–P and Ni–P–Al<sub>2</sub>O<sub>3</sub> composite coatings by reciprocating sliding tests // Wear. – 2019. – **426–427**. – P. 330–340.
- 3. *An overall* aspect of electroless Ni–P depositions / K. Hari Krishnan, S. John, K. N. Srinivasan, J. Praveen, M. Ganesan, and P. M. Kavimani // Metallurgical and Mat. Transact. – 2006. – **37**. – P. 1917–1926.
- 4. *Ashassi-Sorkhabi H. and Rafizadeh S. H.* Effect of coating time and heat treatment on structures and corrosion characteristics of electroless Ni–P alloy deposits // Surf. & Coat. Techn. – 2004. – **176**. –P. 318–326.
- 5. *Anik M., Körpe E., and Sen E.* Effect of coating bath composition on the properties of electroless nickel-boron films // Surf. & Coat. Techn. – 2008. – **202**. –P. 1718–1727.
- 6. *Królikowski A., Karbownicka B., and Jaklewicz O.* Anodic dissolution of amorphous Ni–P alloys // Electrochim. Acta. – 2006. – **51**, № 27. – P. 6120–6127.
- 7. *Corrosion* resistance of electrolessly deposited Ni–P & Ni–W–P alloys with various structures / Y. Gao, Z. J. Zheng, M. Zhu, and C. P. Luo // Mat. Sci. and Eng. – 2004. – **381**. – P. 98–103.
- 8. Preparation and characterization of electroless Ni-P-Fe<sub>3</sub>O<sub>4</sub> composite coating and evaluation of its high temperature oxidation behaviour / A. Zuleta, O. A. Galvis, L. G. Castaño, F. Echeverría, F. Bolívar, M. P. Hierro, F. Pérez-Trujillo // Surf. and Coat. Techn. – 2009. – **203**. – P. 3569–3578.
- 9. *Influence* of heat treatment and oligomeric coatings on the corrosion resistance of amorphous alloys based on aluminum / О. М. Hertsyk, Т. H. Pereverzeva, L. М. Boichyshyn, М. О. Kovbuz, and N. L. Pandyak // Materials Science. – 2019. – **54**, № 4. – P. 526–534.
- 10. *Dmytrakh I. M., Akid R., and Miller K. J.* Electrochemistry of deformed smooth surfaces and short corrosion fatigue crack growth behaviour // British Corr. J. – 1997. – 32,  $\mathbb{N}^2$  2. – P. 138–144.
- 11. *Afroukhteh S., Dehghanian C., and Emamy M.* Preparation of the Ni–P composite coating co-deposited by nano TiC particles and evaluation of it's corrosion property // Appl. Surf. Sci. – 2012. – **258**, № 7. – P. 2597–2601.
- 12. *Electrochemical* studies on eletroless ternary and cuaternary Ni–P based alloys / J. N. Balaraju, V. Ezhil Selvi, V. K. William Grips, and K. S. Rajam // Electrochim. Acta. – 2006. – **52**. – P. 1064–1074.
- 13. *Study* of the corrosion resistance of electroless Ni–P deposits in a sodium chloride medium / G. Rongjie, D. Min, S. Xiaoxia, P. Yanli, and J. Ocean // J. of Ocean University of China. – 2007. – **6**, № 4. – P. 349–354.
- 14. *Bigdeli F. and Allahkaram R. S.* An investigation on corrosion resistance of as-applied and heat treated Ni–P–nanoSiC coatings // Mat. & Des. – 2009. – **30**, № 10. – P. 4450–4453.
- 15. *NiP/SiC composite* coatings: the effects of particles on the electrochemical behavior / C. F. Malfatti, J. Zoppas Ferreira, C. B. Santos, B. V. Souza, E. P. Fallavena, and J. P. Bonino // Corr. Sci. – 2005. – **47**. – P. 567–580.
- 16. *Rabizadeh T., Allahkaram R. S., and Zarebidaki A.* An investigation on effects of heat treatment on corrosion properties of Ni–P electroless nano-coatings // Mat. & Des. – 2010. – **31**, № 7. – P. 3174–3179.
- 17. *Man'ko О. V. and Stets'ko A. E.* Kinetics of the diffusion chromium plating of steels with nickel-cobalt-phosphorus coating // Materials Science. – 2020. – **55**, № 6. – P. 870–877.
- 18. *Structure* and corrosion resistance of Ni–P, Со–Р and Ni–Co–P alloy coatings / K. N. Ignatova, St. V. Kozhukharov, G. V. Avdeev, and I. A. Piroeva // Bulgarian Chem. Commun.  $-2018. -50. -P. 61-69.$
- 19. *Hsu C. H. and Mansfeld F.* Technical note: concerning the conversion of the constant phase element parameter  $y_0$  into a capacitance // Corr.  $- 2001. -57. -P. 747-748.$
- 20. Sankara Narayanana T. S. N., Krishnavenia K., and Seshadrib S. K. Electroless NiP/NiB duplex coatings: preparation and evaluation of microhardness, wear and corrosion resistance // Mat. Chem. and Phys. – 2003. – **82**. – P. 771–779.